

REPORT NO. NADC-78215-60

LEVEL

12

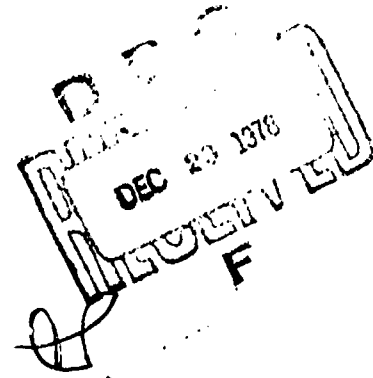


ANALYSIS OF OXYGEN ENRICHED AIR SAMPLES
BY GAS CHROMATOGRAPHY

Lourdes C. Fuller
Aircraft and Crew Systems Technology Directorate
NAVAL AIR DEVELOPMENT CENTER
Warminster, Pennsylvania 18974

10 OCTOBER 1978

PHASE REPORT
AIRTASK NO. A3400000/001C/8W583001
Work Unit No. DS903



APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

Prepared for
NAVAL AIR SYSTEMS COMMAND
Department of the Navy
Washington, D.C. 20361

78 12 28 027

AD A062664

DDC FILE COPY


NOTICES

REPORT NUMBERING SYSTEM - The numbering of technical project reports issued by the Naval Air Development Center is arranged for specific identification purposes. Each number consists of the Center acronym, the calendar year in which the number was assigned, the sequence number of the report within the specific calendar year, and the official 2-digit correspondence code of the Command Office or the Functional Directorate responsible for the report. For example: Report No. NADC-78015-20 indicates the fifteenth Center report for the year 1978, and prepared by the Systems Directorate. The numerical codes are as follows:

CODE	OFFICE OR DIRECTORATE
00	Commander, Naval Air Development Center
01	Technical Director, Naval Air Development Center
02	Comptroller
10	Directorate Command Projects
20	Systems Directorate
30	Sensors & Avionics Technology Directorate
40	Communication & Navigation Technology Directorate
50	Software Computer Directorate
60	Aircraft & Crew Systems Technology Directorate
70	Planning Assessment Resources
80	Engineering Support Group

PRODUCT ENDORSEMENT - The discussion or instructions concerning commercial products herein do not constitute an endorsement by the Government nor do they convey or imply the license or right to use such products.

APPROVED BY:



E. J. STORM
CDR USN
Deputy Director, ACSTD

DATE:

10 October 1978
10 October 1978

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NADC-78215-60	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ANALYSIS OF OXYGEN ENRICHED AIR SAMPLES BY GAS CHROMATOGRAPHY		5. TYPE OF REPORT & PERIOD COVERED PHASE REPORT 1
7. AUTHOR(s) Lourdes C. Fuller		6. PERFORMING ORG. REPORT NUMBER
8. PERFORMING ORGANIZATION NAME AND ADDRESS Aircraft & Crew Systems Technology Directorate Naval Air Development Center Warminster, Pennsylvania 18974		9. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Air Systems Command Department of the Navy Washington, D. C. 20361		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS AIRTASK A3400000/001C/8W0583 001; Work Unit No. DS903
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 10 October 1978
		13. NUMBER OF PAGES 12
		15. SECURITY CLASS. (of this report) Unclassified
		18a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Gas Chromatography Oxygen Analysis Argon Analysis		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The gas chromatograph was used when a method was required to determine the percentages of oxygen and argon in enriched air samples taken from experimental equipment designed to produce pure oxygen aboard an aircraft in flight.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

393 532 78 12 26 027

TABLE OF CONTENTS

	<u>Page No.</u>
LIST OF FIGURES	2
INTRODUCTION.	3
GENERAL DESCRIPTION OF ANALYSIS	3
Determination of Percent Oxygen	3
Determination of Percent Argon	4
CONCLUSIONS	5
RECOMMENDATIONS	5
REFERENCES.	5

ADDITIONAL

DATE

BY

RECEIVED

DISPATCHED

COPIES

SPECIAL

A

L I S T O F F I G U R E S

<u>Figure No.</u>		<u>Page No.</u>
1	Flow Diagram of Oxygen Analysis.	7
2	Chromatograms of Oxygen Analyses	8
3	Flow Diagram of Argon Analysis	9
4	Chromatograms of Argon Analyses.	10

INTRODUCTION

This Center has been involved with the development of systems for producing breathing oxygen from ordinary air aboard an aircraft in flight, eliminating the need to store liquid oxygen. This product should ideally be close to 100% oxygen, but in reality may be somewhat less, and is termed oxygen enriched air. The Aero Materials Laboratory was requested to furnish analytical services to determine the purity of the oxygen enriched air produced by the prototype systems evaluated in Center test facilities, by the Life Support, Protection and Survival Branch of this Directorate. Several types of systems have been tested, including: molecular sieves unit, chlorate candle unit, and fluomine chelate unit.

In each case, the analytical information required included examination of the effluent gas from the test units by infrared spectroscopy to determine trace contaminants present at part per million levels (such as carbon monoxide or methane). Also required were the relative concentrations of the major components of the enriched air sample, which are normally oxygen, argon and nitrogen. In the past two years much progress has been made in this laboratory in the development of an accurate gas chromatographic method to determine percent oxygen, and when necessary, percent argon in enriched air samples.

GENERAL DESCRIPTION OF ANALYSIS

The Hewlett-Packard model 5750 gas chromatograph was used throughout the analyses, equipped with a thermal conductivity detector and a gas sampling valve. The oven, detector and injection port temperatures were held at ambient (25°C). The analytical column was packed with molecular sieves 5A adsorbent. This is a synthetic zeolite material with pore diameters on the order of 5×10^{-8} cm (reference (a)). Molecular sieves are commonly known for their ability to separate the permanent gases, based upon molecular size exclusion and molecular configuration (reference (b)). Oxygen and nitrogen are separated readily. The Van der Waals molecular diameter of oxygen is 2.92×10^{-8} cm; nitrogen is 3.15×10^{-8} cm (reference (c)), the smaller oxygen molecules fitting into the pores of the adsorbent more readily than nitrogen, and therefore moving through the column more slowly. However, oxygen and argon (2.94×10^{-8} cm) are not separable on molecular sieves, except at very long column lengths, due to their similarities in molecular size.

The sampling procedure used for the gas chromatographic analyses was to allow a pressurized sample to flow through the loop of the gas sampling valve at a flow rate of approximately 60 ml/min. Several injections were made for each sample. An equal number of standard injections were made, preferably immediately before and after the sample injections. The values obtained for separate injections were averaged to be used in the percent calculations.

DETERMINATION OF PERCENT OXYGEN

For this analysis, helium was used as the carrier gas, with a flow rate of 40 ml/min. The optimum loop volume for the gas sampling valve was

approximately 200 μ l. This volume gave a reproducible oxygen peak on the chart paper or integrator without overloading the capacity of the column, and without the need for the use of high attenuation.

The oxygen and any argon in the sample emerge from the detector as one peak, separated from the peak due to nitrogen, if nitrogen is present (Figures 1 and 2). The initial quantitation was done using the height of the oxygen/argon peak since, under the experimental conditions used, the oxygen/argon peak emerged as a spike on the chart paper, and peak height was found to be linear with concentration. After the initial work had been completed, a graphic integrator was acquired, and now all calculations are based on integrated peak area.

For samples of enriched air generated by other than a molecular sieves unit, where the concentration of oxygen relative to nitrogen was large, the contribution of argon to the oxygen/argon peak was found to be negligible.

For samples generated by the molecular sieves units, however, it was assumed that the argon would be concentrated in the same proportions as the oxygen since the same factors which prevent the analytical separation of oxygen and argon would tend to concentrate them in the same proportions.

Before the method for determining argon was developed, the argon concentration could only be estimated using the relative concentrations of the two gases in normal air:

$$\frac{[O_2]}{[Ar]} = \frac{20.946\%}{0.934\%}$$

$$[O_2] + [Ar] = \% \text{ determined by } O_2/Ar \text{ peak} \quad (1)$$

$$[Ar] = \frac{[O_2] [0.934]}{[20.946]} \quad (2)$$

Using the equations (1) and (2), the theoretical percentage of the argon component was calculated, and then subtracted from the value determined from the combined oxygen/argon peak, to determine percent oxygen. Now that the method for determining argon directly is available, a more accurate value is derived for percent oxygen.

The standards on which calculations were made were pure oxygen (99.99% O_2 , negligible Ar and N_2) for samples with high oxygen concentration; and room air (20.946% O_2 , 0.934% Ar, and 78.084% N_2) for low oxygen containing samples.

DETERMINATION OF PERCENT ARGON

The conditions for determining argon concentration are more complicated than those for determining oxygen (reference (d), Figures 3 and 4). Hydrogen is used as the carrier gas for this analysis, with a flow rate of approximately 60 ml/min. The carrier gas plus sample passes first through a stainless steel column filled with a commercially available catalyst, 25-40 mesh size. All of the oxygen in the sample reacts with the hydrogen carrier gas to

form water in the presence of this catalyst (a precious metal alloy of the platinum group deposited on alumina). The second column is filled with molecular sieves 13X. The purpose of this column is to absorb the water generated in the first column, while allowing any argon or nitrogen present to pass through. The last column is the analytical column, filled with molecular sieves 5A, after which argon and nitrogen pass through the detector as separate peaks.

A large sample loop volume (approximately 2 ml) is needed for a direct determination of argon. Two variables were considered in the choice of the proper sample size. A sufficient volume is needed to provide enough sensitivity of detector response so that reproducible peak areas can be calculated. This is quite important for quantitation since the argon component is present at less than 5% of the total sample volume. The other factor is that a minimum sample volume is desired since a certain amount of water is generated after each sample injection. The accumulation of water eventually deactivates the catalyst and adds irreversibly to the molecular sieves columns. The smaller the sample size, the longer the columns will be useful.

The standards used for calculation of percent argon are a commercially prepared calibration mixture (4.61% Ar, 95.39% O₂), room air (0.934% Ar, 20.946% O₂, 78.084% N₂), and pure oxygen (containing no argon). The pure oxygen is used during each analysis to verify that all oxygen is being catalytically reacted and removed from the gas stream.

C O N C L U S I O N S

The initial quick-response analyses to determine percent oxygen enabled personnel in the Life Support, Protection and Survival Branch to monitor the capabilities of their enriched air generating units during testing. Due to recent modifications of the analytical equipment and the addition of a graphic integrator, argon can also be determined quantitatively and even more reliable results for percent oxygen can be obtained.

R E C O M M E N D A T I O N S

It is recommended that the procedures described above be considered whenever methods are required for determining oxygen and argon in oxygen enriched air. They are low cost techniques, feasible for use with any gas chromatograph equipped with a thermal conductivity detector.

If the volume of sampling is expected to continue, it is recommended that additional modifications be made to the gas chromatograph in order to ease the switching of carrier gases between the oxygen and argon analyses. Also important in cutting down analysis time would be the installation of an additional sampling valve.

R E F E R E N C E S

- a. Gordon, A. J., and Ford, R. A., The Chemist's Companion, John Wiley & Sons, New York, 1972, p. 447
- b. McNair, H. M. and Bonelli, E. J., Basic Gas Chromatography, 5th ed., Varian Aerograph, Palo Alto, CA, 1969, p. 69

- c. Weast, R. C., ed., Handbook of Chemistry and Physics, 51st ed., Chemical Rubber Co., Cleveland, OH, 1970, p. F-151
- d. Private correspondences with H. E. Lindenmoyer, Specialty Gas Department, Air Products and Chemicals, Inc., telecon 17 Dec 76, and letter 27 Dec 76

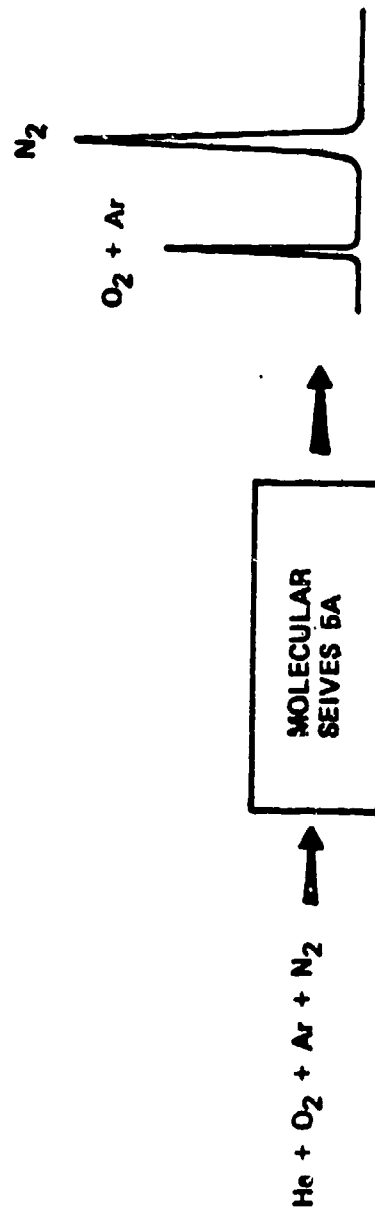


FIGURE 1. Flow Diagram of Oxygen Analysis

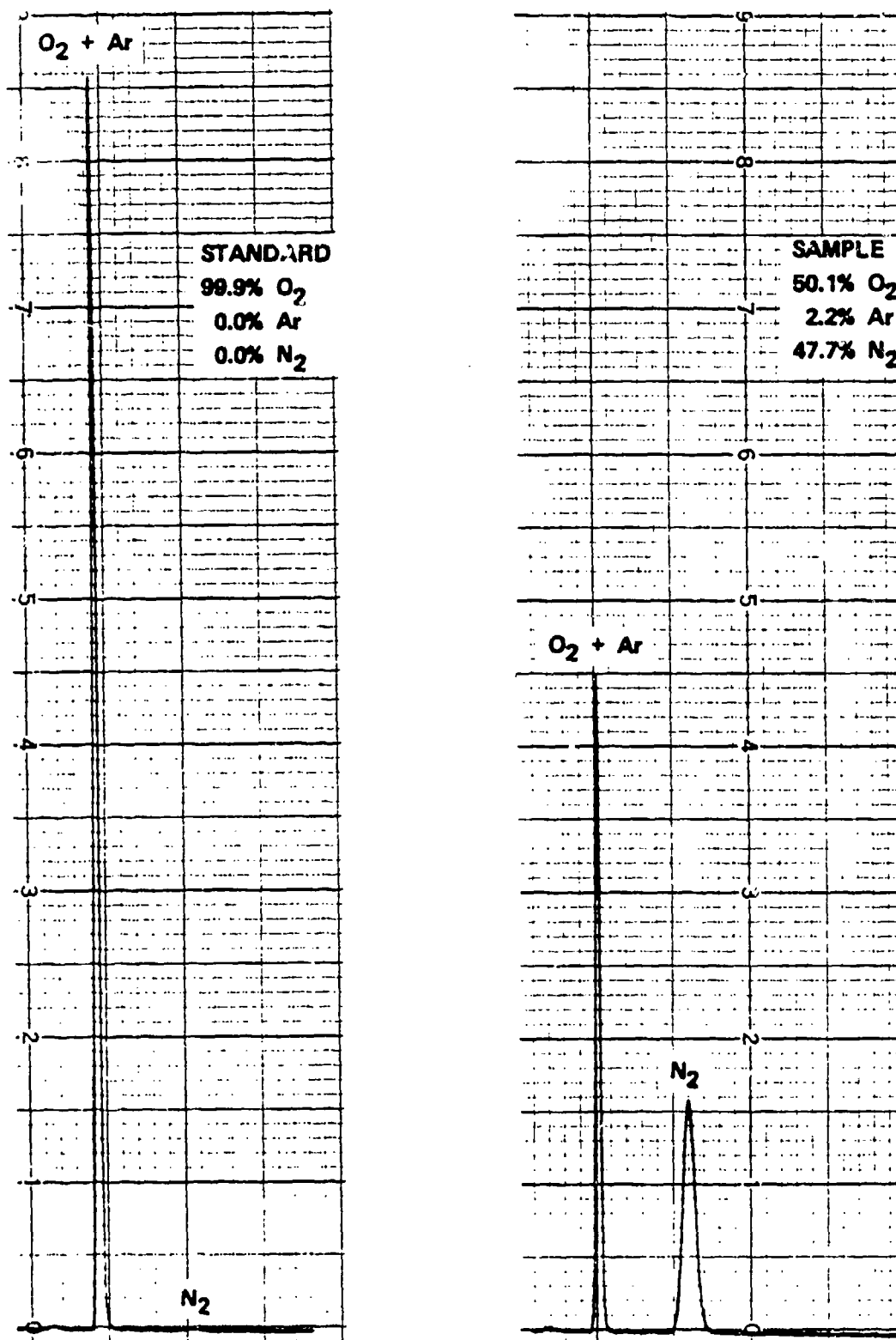


FIGURE 2. Chromatograms of Oxygen Analyses

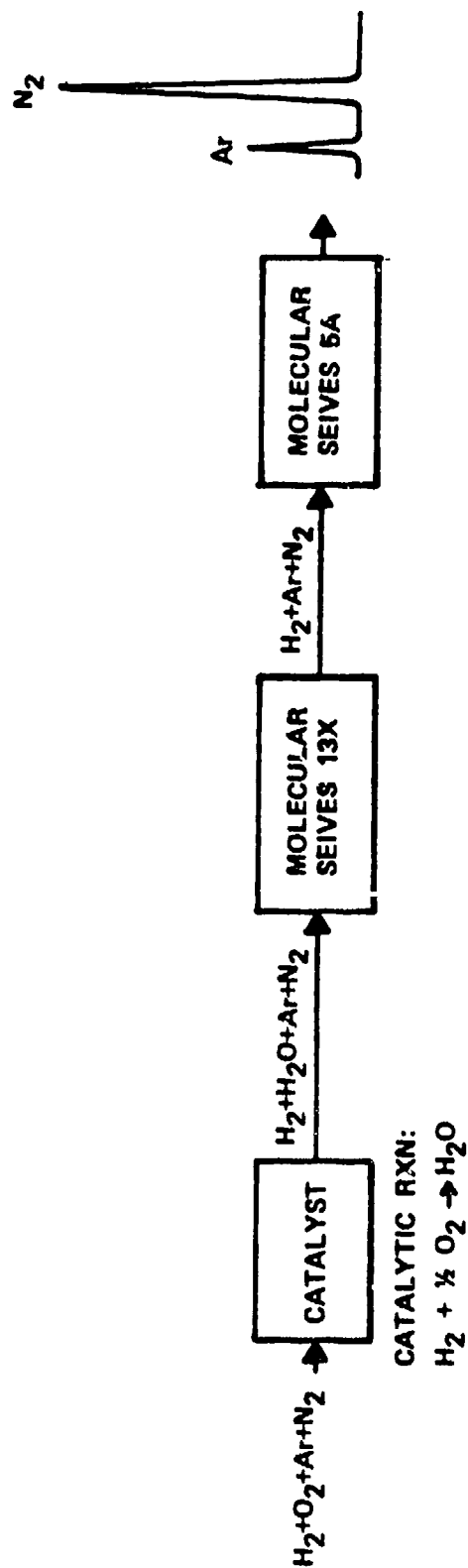


FIGURE 3. Flow Diagram of Argon Analysis

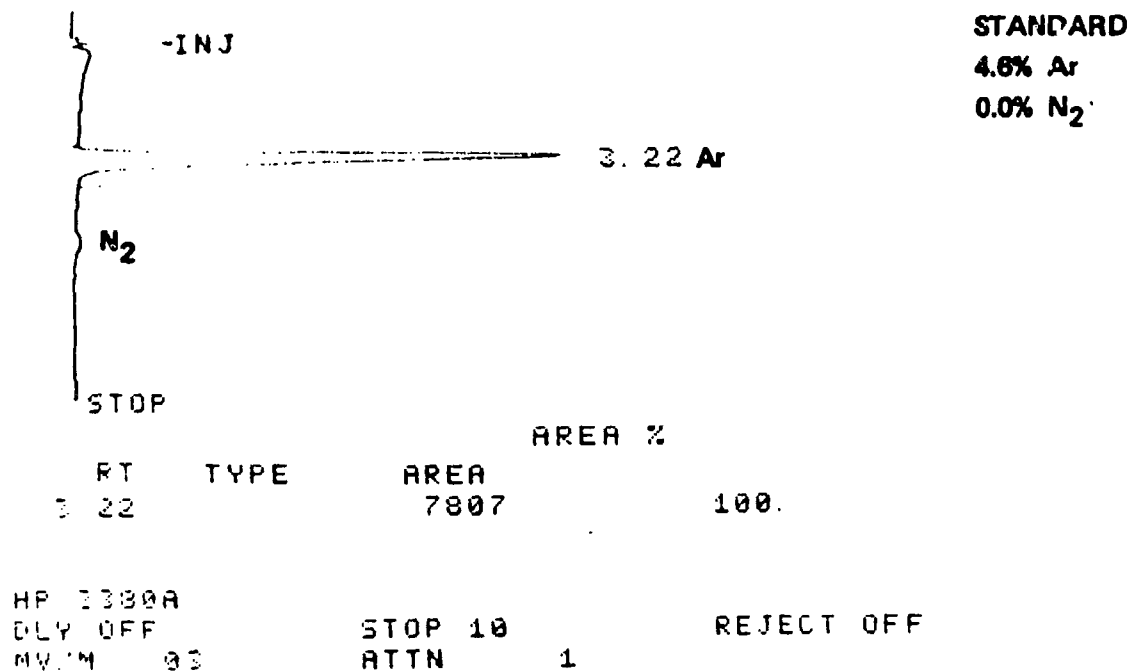
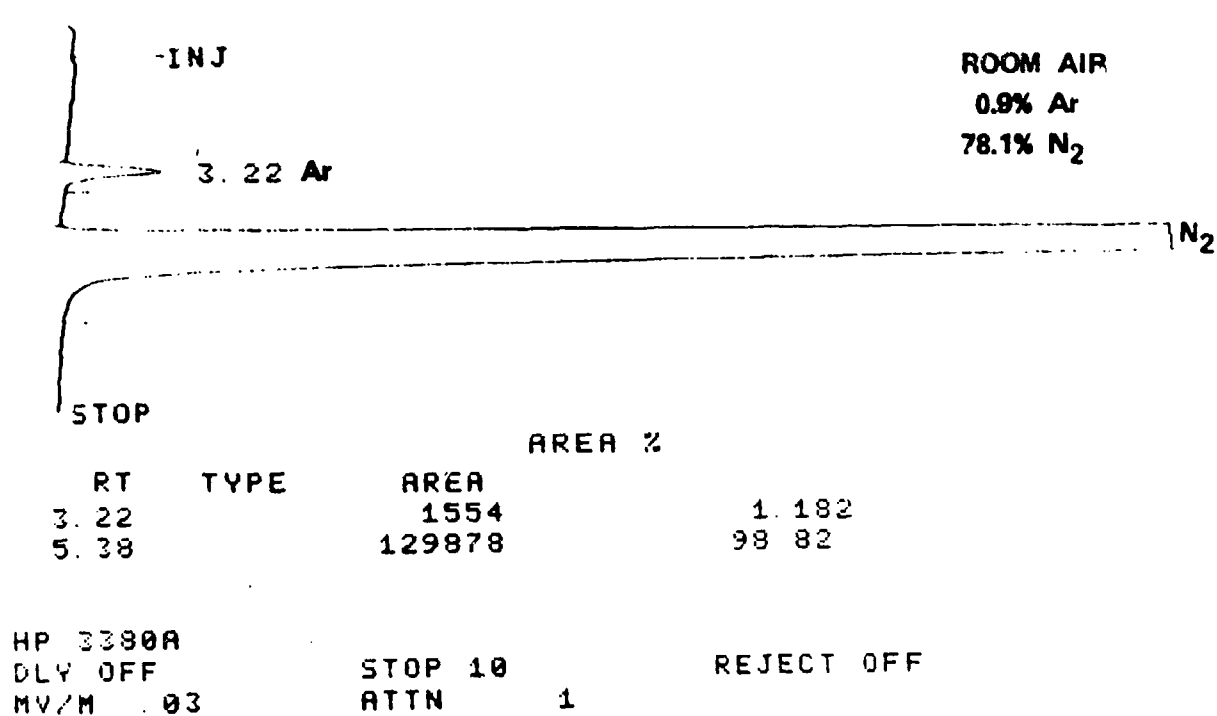


FIGURE 4. Chromatograms of Argon Analyses

NADC-78215-60

D I S T R I B U T I O N L I S T

AIRTASK NO. A3400000/001C/8W583001
Work Unit No. DS903

	<u>No. of Copies</u>
NAVAIR (AIR-950D)	18
2 for retention	
2 for AIR-5203	
2 for AIR-52032	
2 for AIR-52032B	
2 for AIR-531A	
2 for AIR-5311B	
2 for AIR-4173	
2 for AIR-414D	
2 for AIR-340B	
COMNAVAIREPLANT	2
NAVAVNLOGCEN	2
NAVAIRENGCEN (ESSD 92714)	2
NAVAIREWORKFAC, Alameda	1
Jacksonville	1
Norfolk	1
North Island	1
Pensacola	1
MCAS, Cherry Point	1
KELLY AFB, (SQA), San Antonio, TX	2
BROOKS AFB, (VNL), San Antonio, TX	2
WPAFB, (SFQLA), Ohio	2
DDC	12